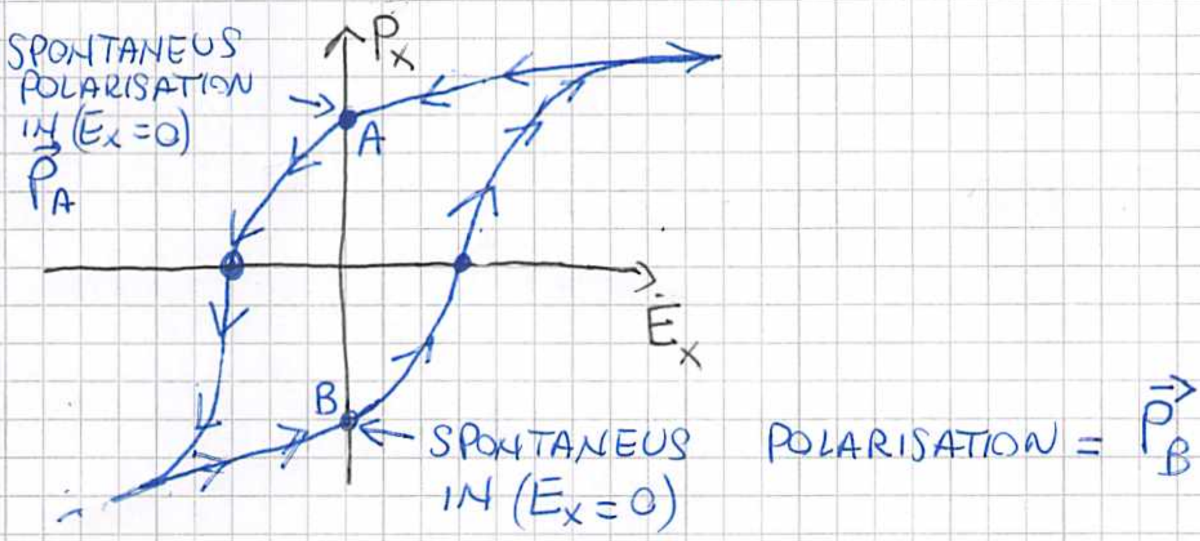
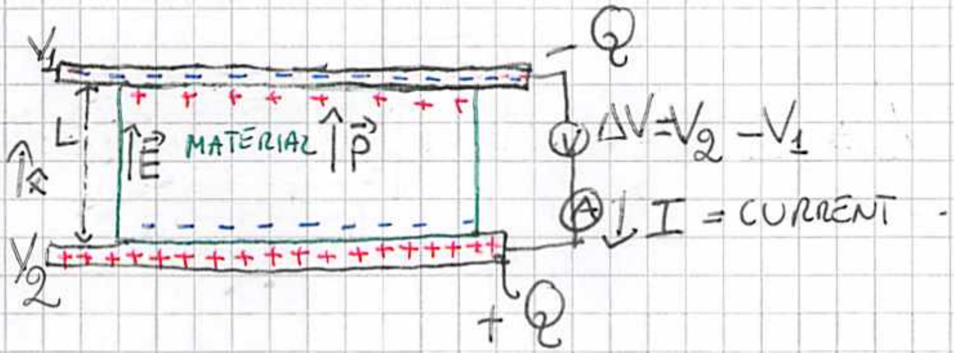
# FERROELECTRICITY




$$E_x = \frac{\Delta V}{L}$$

SURFACE CHARGE IN THE MATERIAL (UPPER SURFACE)

NORMAL TO THE SURFACE

$$\vec{P}\cdot\hat{n} = P_x$$

SURFACE CHARGE ON THE METAL PLATE

$$\frac{Q}{A}$$

$Q$ → TOTAL CHARGE ON THE UPPER METAL PLATE

$A$ → AREA OF THE METAL PLATE

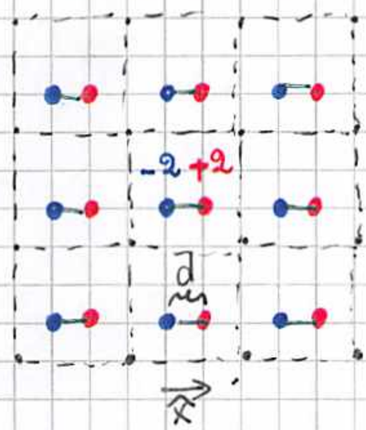
FOR THE GAUSS THEOREM

$$E_x = -4\pi\left(P_x - \frac{Q}{A}\right)$$

$$P_x = \frac{Q}{A} - \frac{\Delta V}{4\pi L} \qquad Q(E_A) - Q(E_B) = \int_{t_A}^{t_B} dt\, I(t)$$

# MICROSCOPIC PICTURE WITH POINT CHARGES

MOLECULAR CRYSTAL (GEDANKEN FERROELECTRIC) $\overset{+2}{C} \equiv \overset{-2}{O}$ MOLECULE




$$\vec{P} = \frac{2|e|d}{V_{\text{UNIT CELL}}}\hat{x}$$

EXAMPLES OF REAL FERROELECTRICS

$PbTiO_3$, $BaTiO_3$, $SnTe$, ...

# DIPOLE MOMENT IN A MOLECULE

$$\vec{d} = -|e|\int d^3r \, \rho(\vec{r})\,\vec{r} \; + |e|\sum_I Z_I \vec{R}_I$$

ELECTRONIC CHARGE

IS THE DIPOLE MOMENT PER UNIT VOLUME IN A PERIODIC INSULATING SOLID A BULK PROPERTY? YES (BUT THE ANSWER WAS GIVEN JUST IN 1993 (KING-SMITH VANDERBILT))

- FOR SEMPLICITY LET'S CONSIDER A ONE DIMENTIONAL PERIODIC SOLID

FIRST CASE A SOLID WITH CLASSICAL ELECTRON FROZEN IN SPACE (THE CHARGES ARE QUANTIZED)

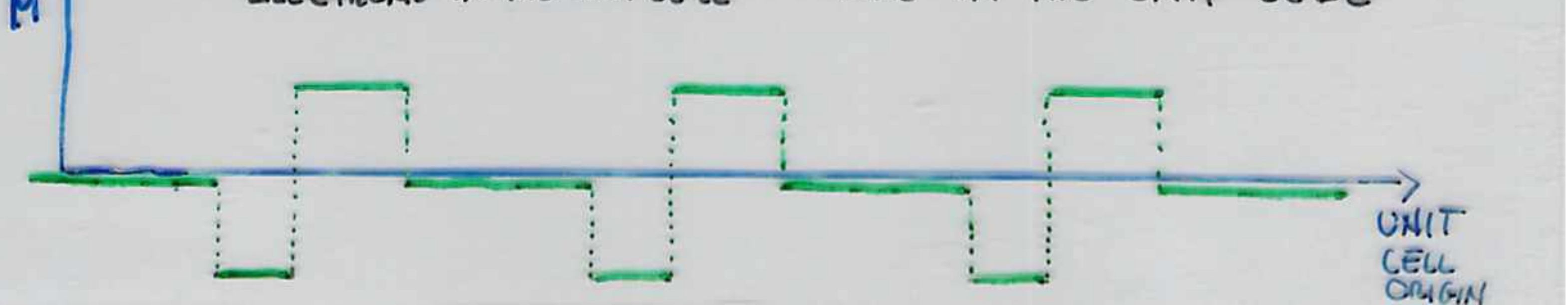
CATAION CHARGE $+2|e|$


ELECTRONS CHARGE $-|e|$

A POSSIBLE CHOICE OF THE UNIT CELL (L ≡ LENGHT OF THE UNIT CELL

$$M \equiv \frac{1}{L}\left[-|e|\sum_i x_i \; + |e|\sum_I Z_I x_I\right]$$

ELECTRONS IN THE UNIT CELL — IONS IN THE UNIT CELL



THE POLARIZATION DEPENDS ON THE CELL CHOICE WITH CLASSICAL FROZEN ELECTRON M IS DEFINED MODULUS $|e|$.

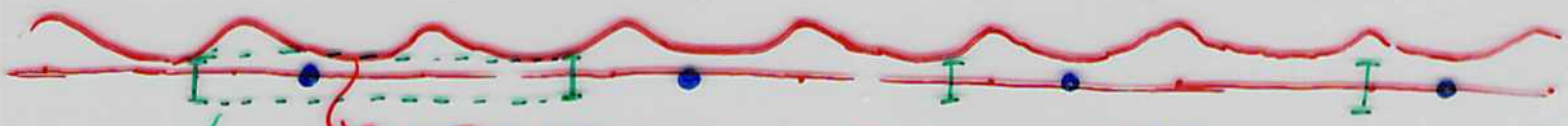
I.E. CHAINGING THE CELL CHOICE $M \to M' = M' + |e| j$

WITH $j$ = POSITIVE OR NEGATIVE INTEGER

THIS IS NOT A BIG PROBLEM SINCE USUALLY CHANGE OF POLARIZATION IS MEASURED (WHEN E.G. THE IONS ARE MOVED) AND IT IS SUFFICIENT THAT THE CELL IS CHOSEN IN SUCH A WAY THAT $M(t)$ DOES NOT JUMP DURING THE TRANSFORMATION

SECOND CASE SOLID WITH QUANTUM ELECTRONS

CATAPN CHARGE $+2|e|$

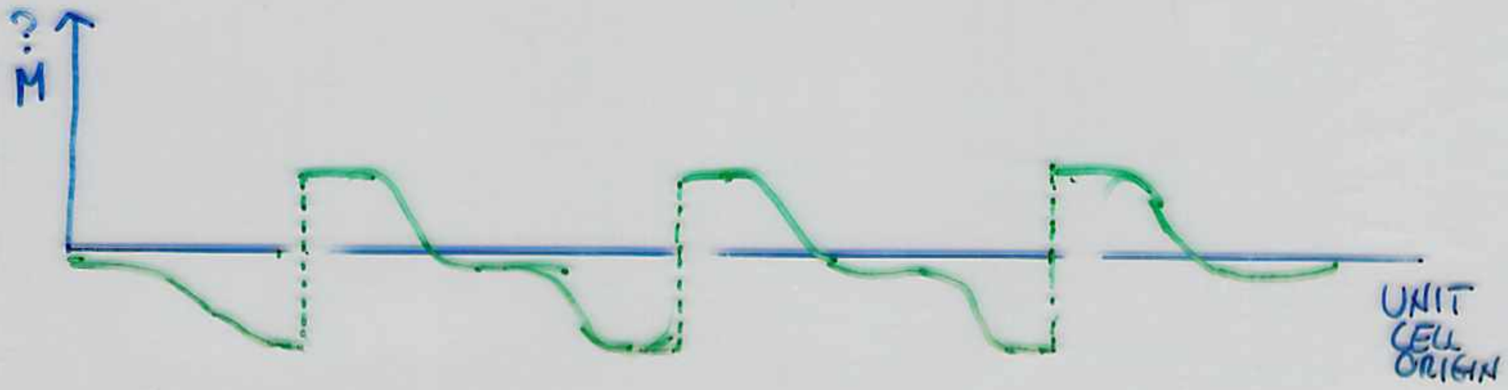


ELECTRONIC CHARGE DENSITY $n(x)$

POSSIBLE CHOICE OF THE UNIT CELL

$$M \stackrel{?}{=} \frac{1}{L}\left[ -|e| \int_{\substack{\text{UNIT}\\ \text{CELL}}} dx\, n(x)\, x + |e| \sum_I Z_I x_I \right]$$

$I$ ← IONS IN THE UNIT CELL



IN A 3D SOLID POLARISATION DEFINE UP TO A VECTOR

$$\frac{e\vec{R}}{V_{\text{UNIT CELL}}} \qquad \vec{R} \in \text{DIRECT LATTICE}$$

# MACROSCOPIC POLARISATION AS A BERRY PHASE

[KING-SMITH AND VANDERBILT PRB 47, R1651 (1993)]

ATOMS IN THE A POSITION

ATOMS IN THE B POSITION

WE HAVE A WELL DEFINED EXPRESSION FOR THIS

$$\vec{P}(\lambda_A) - \vec{P}(\lambda_B) = \int_{\lambda_B}^{\lambda_A} d\lambda \, \frac{d\vec{P}}{d\lambda}$$

$$\doteq \underset{\text{BERRY}}{F}\left[\{\psi_{\vec{k}i}^{\lambda_A}\}_{i\,occ}\right] - \underset{\text{BERRY}}{F}\left[\{\psi_{\vec{k}i}^{\lambda_B}\}\right]$$

# WHAT IS A BERRY PHASE?

[BERRY, PROC. ROY. SOC. LOND. A 392, 45 (1984)
RESTA, J. PHYS. COND-MAT 12, R107 (2000)]

- BERRY PHASE OBSERVABLE THAT CANNOT BE CAST AS EXPECTATION OF AN OBSERVABLE

$H_{\vec{\eta}}$ HAMILTONIAN THAT DEPEND ON A PARAMETER $\vec{\eta}$

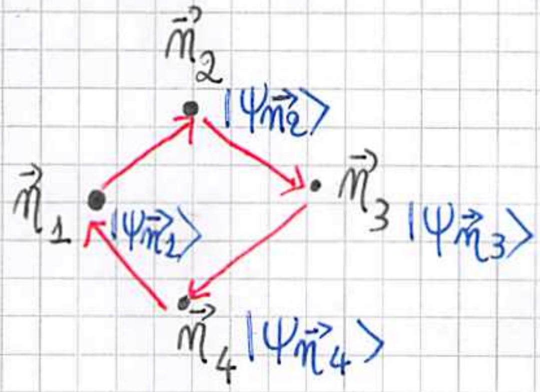
EXAMPLES – $\vec{\eta}$ ATOMIC COORDINATES IN B.O. APPROXIMATION

– $\vec{k}$ IN $H_{\vec{k}}$ HAMILTONIAN

$\vec{\eta} \in$ SET OF VALUES :

$|\psi_{\vec{\eta}}\rangle$ NON DEGENERATE GROUND STATE OF $H_{\vec{\eta}}$

LET'S CONSIDER A FINITE NUMBER OF POINTS IN $\vec{\eta}$ SPACE



$\Delta\varphi_{12} \equiv$ PHASE DIFFERENCE BETWEEN THE GROUND STATES IN THE 2 POINTS $\equiv -\mathrm{Im}\left[\ln\left(\langle\psi_{\vec{n}_1}|\psi_{\vec{n}_2}\rangle\right)\right]$

$$\Downarrow$$

$$e^{-i\Delta\varphi_{12}} = \frac{\langle\psi_{\vec{n}_1}|\psi_{\vec{n}_2}\rangle}{|\langle\psi_{\vec{n}_1}|\psi_{\vec{n}_2}\rangle|}$$

$\Delta\varphi_{12} \to$ NO PHYSICAL MEANING SINCE

IF $|\psi_{\vec{n}_2}\rangle$ EIGENSTATE OF $H_{\vec{n}_2}$

$\to e^{ia}|\psi_{\vec{n}_2}\rangle$ " "

$$\Delta\varphi_{12} \to \Delta\varphi_{12} - a$$

- FOR A CLOSED LOOP

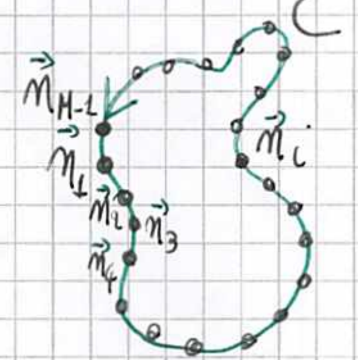
$$\varphi = \Delta\varphi_{12} + \Delta\varphi_{23} + \Delta\varphi_{34} + \Delta\varphi_{41}$$

$$= -\mathrm{Im}\left[\ln\left(\langle\psi_{\vec{n}_1}|\psi_{\vec{n}_2}\rangle\langle\psi_{\vec{n}_2}|\psi_{\vec{n}_3}\rangle\langle\psi_{\vec{n}_3}|\psi_{\vec{n}_4}\rangle\langle\psi_{\vec{n}_4}|\psi_{\vec{n}_2}\rangle\right)\right]$$

BY $|\psi_2\rangle \to e^{ia}|\psi_2\rangle$ $\times e^{ia}$ $\times e^{-a}$ THE PHASES CANCEL OUT

- $\varphi$ PHASE INVARIANT (IT COULD BE ASSOCIATED TO AN OBSERVABLE)

# CONTINOUS PATH IN $\vec{\eta}$ SPACE




$i = 1, M-1$

$|\psi_{\vec{\eta}_M}\rangle = |\psi_{\vec{\eta}_1}\rangle$ [O PIÙ IN GENERALE $|\psi_{\vec{\eta}_M}\rangle = f(|\psi_{\vec{\eta}_2}\rangle)$]

FUNZIONALE DETERMINISTICO E DIFFERENZIABILE

$$\varphi = \lim_{\substack{M\to\infty \\ \forall i\, |\vec{\eta}_{i+1}-\vec{\eta}_i| \to 0}} \sum_{i=1}^{M-1} \Delta\varphi_{i,i+1} \stackrel{def}{\equiv} \oint_C d\varphi$$

IF THE PHASE-GAUGE IS CHOSEN IN SUCH A WAY THAT $|\psi_{\vec{\eta}}\rangle$ DIFFERENTIABLE WITH RESPECT TO $\eta$

$$\langle\psi_{\vec{\eta}_i}|\psi_{\vec{\eta}_{i+1}}\rangle = \underbrace{\langle\psi_{\vec{\eta}_i}|\psi_{\vec{\eta}_i}\rangle}_{=1} + \underbrace{\langle\psi_{\vec{\eta}_i}|\frac{d|\psi_{\vec{\eta}_i}\rangle}{d\vec{\eta}_i}}_{ia}(\vec{\eta}_{i+1}-\vec{\eta}_i) + O(\Delta\eta^2)$$

$a \in$ REAL

BY TAYOR EXPANSION OF THE $\ln(1+ia)$

$$\Delta\varphi_{i,i+1} = -\Im m\left[\ln\left(\langle\psi_{\vec{\eta}_i}|\psi_{\vec{\eta}_{i+1}}\rangle\right)\right] \stackrel{\downarrow}{=} +i\langle\psi_{\vec{\eta}_i}|\frac{\partial|\psi_{\vec{\eta}_i}\rangle}{\partial\vec{\eta}}\cdot(\vec{\eta}_{i+1}-\vec{\eta}_i)$$

$$\boxed{\varphi = \text{BERRY PHASE} = \oint_C \vec{A}\cdot d\vec{\eta} \qquad \vec{A}(\vec{\eta}) = i\langle\psi_{\vec{\eta}}|\frac{d\psi}{d\vec{\eta}}\rangle = \text{BERRY CONNECTION}}$$

MANIFESTATIONS OF BERRY PHASES

- AHARONOV-BOHN EFFECT (A.B.)
- MOLECULAR AB ($Li_3$)
- ADIABATIC APPROXIMATION IN $\vec{B}$ FIELD
- ......
- POLARISATION

NOTE THAT THE BERRY PHASE IS DEFINED MODULUS A PHASE $2\pi j$ WITH $j$ INTEGER INDEED:

STILL PERIODIC ON THE CLOSED LOOP

$$|\psi_{\vec{n}_i}\rangle \rightarrow e^{-i(2\pi j \frac{i}{M-1})} |\psi_{\vec{n}_i}\rangle$$

$$\varphi \rightarrow \varphi + 2\pi j$$

# WANNIER FUNCTIONS OF A PERIODIC SOLID

(FOR SIMPLICITY WE CONSIDER ONE BAND, OR ONE BAND DISCONNECTED FROM THE OTHERS)

- IN DFT GROUND STATE PROPERTIES CAN BE OBTAINED FROM THE PROJECTOR OVER OCCUPIED STATES

$$P = \sum_{\vec{k}} |\psi_{\vec{k}}\rangle\langle\psi_{\vec{k}}|$$

WHERE $\langle\psi_{\vec{k}}|\psi_{\vec{k}'}\rangle \overset{N\text{-CELLS}}{=} \delta_{\vec{k},\vec{k}'}$ $\quad |\psi_{\vec{k}}\rangle = \frac{e^{i\vec{k}\vec{r}}}{\sqrt{N}}|u_{\vec{k}}\rangle$

$\langle u_{\vec{k}}|u_{\vec{k}}\rangle \overset{\text{UNIT CELL}}{=} 1$

- UNITARY ROTATION IN THE OCCUPIED STATE

$\vec{R} \in$ SITES INSIDE SUPERCELL

$$|w_{\vec{R}}\rangle \overset{def}{\equiv} \text{WANNIER FUNCTION OF SITE } \vec{R} \overset{def}{\equiv} \sum_{\vec{k}} \frac{e^{-i\vec{k}\cdot\vec{R}}}{\sqrt{N}}|\psi_{\vec{k}}\rangle = \sum_{\vec{k}} \underbrace{U_{\vec{R}\vec{k}}}_{N\times N \text{ UNITARY MATRIX}} |\psi_{\vec{k}}\rangle$$

$\vec{R}$ SITES INSIDE THE N-CELL SUPERCELL

$$P = \sum_{\vec{k}} |\psi_{\vec{k}}\rangle\langle\psi_{\vec{k}}| = \sum_{\vec{R}} |w_{\vec{R}}\rangle\langle w_{\vec{R}}|$$

$$\Downarrow$$

FOR ANY OBSERVABLE $O$

$$\sum_{\vec{k}} \langle\psi_{\vec{k}}|O|\psi_{\vec{k}}\rangle = \sum_{\vec{R}} \langle w_{\vec{R}}|O|w_{\vec{R}}\rangle$$

# PROPERTIES OF WANNIER FUNCTIONS

- $$\langle W_{\vec{R}} | W_{\vec{R}'} \rangle = \sum_{\vec{k}} U^*_{\vec{R}\vec{k}} U_{\vec{R}'\vec{k}} = \frac{\sum e^{i\vec{k}(\vec{R}'-\vec{R})}}{N} \cdot = \delta_{\vec{R},\vec{R}'}$$

WANNIER FUNCTION ARE ORTHONORMAL

- $$\langle \vec{r}+\vec{R} | W_{\vec{R}} \rangle = \sum_{\vec{k}} \frac{e^{-i\vec{k}\cdot\vec{R}}}{\sqrt{N}} \langle \vec{r}+\vec{R} | \psi_{\vec{k}} \rangle = \sum_{\vec{k}} \frac{e^{-i\vec{k}\cdot\vec{R}}}{\sqrt{N}} e^{+i\vec{k}\cdot\vec{R}} \langle \vec{r} | \psi_{\vec{k}} \rangle$$
$$= \sum_{\vec{k}} \langle \vec{r} | \psi_{\vec{k}} \rangle = \langle \vec{r} | W_{\vec{0}} \rangle$$

THE WANNIER FUNCTION OF SITE $\vec{R}$ IS OBTAINED AS A TRANSTATION BY $\vec{R}$ OF THAT OF SITE $\vec{0}$

- SINCE THE PHASE OF BLOCH FUNCTION IS ARBITRARY THE WANNIER FUNCTION ARE ARBITRARY

$$|\psi'_{\vec{k}}\rangle = e^{i\gamma(\vec{k})} |\psi_{\vec{k}}\rangle$$ WHERE :
- $\gamma(\vec{k}) \in$ REAL
- $e^{i\gamma(\vec{k})}$ PERIODIC FUNCTION WITH RESPECT TO $\vec{G}$:

$$e^{i\gamma(\vec{k}+\vec{G})} = e^{i\gamma(\vec{k})}$$

$$|W'_{\vec{R}}\rangle = \sum_{\vec{k}} \frac{e^{-i\left[\vec{R}\cdot\vec{k} - \gamma(\vec{k})\right]}}{\sqrt{N}} |\psi_{\vec{k}}\rangle$$ = DIFFERENT NOT JUST BY A GLOBAL PHASE

CONJECTUR DEMOSTRATED IN 3D ONLY
IN (BROUDER, PANATI, CALANDRA, MOUROUGANE, MARZARI
PRL $\underline{98}$, 046402, (2007))

BY AN APPROPIATE CHOICE OF THE PHASE
FACTOR $\gamma(\vec{k})$ FOR $N \to \infty$ $\langle \vec{r} | W_{\vec{R}} \rangle$
ARE EXPONENTIALLY LOCALIZED IN REAL SPACE
IF WE CONSIDER BLOCH STATE PERIODIC
IN $\vec{G}$ NAMELY

$$\boxed{|\psi_{\vec{k}+\vec{G}}\rangle = |\psi_{\vec{k}}\rangle} \quad \forall \vec{G} \in \text{RECIPROCAL LATTICE VECTOR}$$

$$\Downarrow$$

$$\boxed{|u_{\vec{k}+\vec{G}}\rangle = e^{-i\vec{G}\cdot\vec{r}} |u_{\vec{k}}\rangle}$$

# EXPECTATION VALUE OF THE POSITION OPERATOR IN SOLIDS

$\langle \psi_{\vec{k}} | \vec{r} | \psi_{\vec{k}} \rangle$ NOT WELL DEFINED SINCE $\langle r | \psi_{\vec{k}} \rangle$ DELOCALIZED OVER WHOLE SPACE

$\langle \vec{r} | W_R \rangle$ IS EXPONENTIALLY LOCALIZED (FOR $N \to \infty$)

$\Downarrow$

WELL DEFINED FOR $N \to \infty$

$$\langle W_{\vec{R}} | \vec{r} | W_{\vec{R}} \rangle = \vec{r}_W + \vec{R}$$

WANNIER CENTER OF $|W_{\vec{0}}\rangle$

HOW DOES $\vec{r}_W$ DEPEND ON THE (GAUGE) ARBITRARY PHASE $\gamma(\vec{k})$?

$$\vec{r} | \psi_{\vec{k}} \rangle = \frac{d}{i\, d\vec{k}} \left( \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{N}} | u_k \rangle \right) - \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{N}} \frac{d\, | u_{\vec{k}} \rangle}{i\, d\vec{k}}$$

SUPERCELL

$$\langle W_{\vec{0}} | \vec{r} | W_{\vec{0}} \rangle = \sum_{\vec{k}\vec{k}'} \Big[ \langle u_{\vec{k}'} | \frac{e^{-i\vec{k}'\vec{r}}}{N} \frac{d}{i\, d\vec{k}} \frac{e^{i\vec{k}\cdot\vec{r}}}{N} | u_{\vec{k}} \rangle$$

SUPERCELL

$$- \langle u_{\vec{k}} | \frac{e^{-i\vec{k}'\vec{r}}}{N} \frac{e^{i\vec{k}\vec{r}}}{N} | \frac{d\, | u_{\vec{k}} \rangle}{d\vec{k}}$$

FIRST TERM $(N \to \infty)$

UNIT CELL VOLUME

$$= \langle W_0 | V \int \frac{d^3k}{(2\pi)^3} \frac{d}{i\,d\vec{k}} \underbrace{\left[ \overbrace{e^{i\vec{k}\cdot\vec{r}}}^{\text{PERIODIC FUNCTION WITH RESPECT TO THE } \vec{k} \text{ INDEX AS } |\psi_{\vec{k}}\rangle} |u_{\vec{k}}\rangle \right]}_{\text{TOTAL DERIVATIVE OF PERIODIC FUNCTION}} =$$

NOT NORMALIZABLE (NOT $\mathbb{L}^2$) BUT OK SINCE $\langle W_0 | \vec{r} \rangle$ LOCALIZED

$= 0$ INTEGRAL OF A TOTAL DERIVATIVE OF A PERIODIC FUNCTION

SECOND TERM

SUPERCELL

$$= - \sum_{\vec{R}} \int_{\text{UNIT CELL}} d^3r \sum_{\vec{k}\vec{k}'} \overbrace{\langle u_{\vec{k}'} | \vec{r} \rangle \langle \vec{r} | \frac{d\, |u_{\vec{k}}\rangle}{i\,d\vec{k}} \frac{e^{i(\vec{k}-\vec{k}')\vec{r}}}{N} \frac{e^{i(\vec{k}-\vec{k}')\vec{R}}}{N}}^{\delta_{\vec{k},\vec{k}'}}$$

$$= +i \frac{1}{N} \sum_{\vec{k}} \langle u_{\vec{k}} | \frac{d u_k}{d\vec{k}} \rangle$$

$N \to \infty$

$$\boxed{\langle W_{\vec{0}} | \vec{r} | W_{\vec{0}} \rangle = \vec{r}_W = i \, \overbrace{V \int \frac{d^3k}{(2\pi)^3} \langle u_{\vec{k}} | \frac{d u_{\vec{k}}}{d\vec{k}} \rangle}^{\text{BERRY PHASE}}}$$

1D FOR SIMPLICITY

UNIT CELL

$$\langle W_0 | x | W_0 \rangle = \frac{L}{2\pi} \underbrace{\int dk \, i \langle u_k | \frac{d u_k}{dk} \rangle}_{\text{BERRY PHASE} = \varphi + 2\pi j}$$

INTEGER

$$= L \frac{\varphi}{2\pi} + L \cdot j$$

THE CENTROID IS WELL DEFINE AN INDEP OF THE PHASE GAUGE $\gamma(\vec{k})$ A PART A DIRECT LATTICE VECTOR

BASIS FOR DIRECT LATTICE

INTEGER

IN 3D $\langle W_{\vec{0}} | \vec{r} | W_{\vec{0}} \rangle = \vec{a}_1 \left( \frac{\varphi_1}{2\pi} + j_1 \right) + \vec{a}_2 \left( \frac{\varphi_2}{2\pi} + j_2 \right) + \vec{a}_3 \left( \frac{\varphi_3}{2\pi} + j_3 \right)$

# MACROSCOPIC POLARISATION OF A SOLID (INSULATOR)

$$\vec{P} = \frac{1}{\underset{\text{UNIT CELL VOLUME}}{V}} \left[ \sum_{i}^{\substack{\text{OCCUPIED}\\ \text{BANDS}}} - \overset{\text{SPIN}}{2} |e| \underbrace{\langle W_{\vec{0}i} | \vec{r} | W_{\vec{0}i} \rangle}_{\substack{\text{CENTROID OF WANNIER}\\ \text{FUNCTION OF BAND } i}} + \sum_{\alpha}^{\substack{\text{ATOMS}\\ \text{UNIT CELL}}} |e| Z_\alpha \vec{r}_\alpha \right]$$

IN AN INSULATOR

- ELECTRONS ARE LIKE POINT CHARGES LOCALIZED AT THE CENTROID POSITION

# POLARIZATION BY INTEGRATING THE PERTURBATION

$$\vec{P}(\lambda_A) - \vec{P}(\lambda_B) = \int_{\lambda_B}^{\lambda_A} d\lambda \, \frac{d\vec{P}}{d\lambda} =$$

$$= -2|e| i \int_{\lambda_B}^{\lambda_A} d\lambda \int \frac{d^3k}{(2\pi)^3} \sum_i^{occ} \left[ \frac{d\langle u_{\vec{k}i}|}{d\lambda} \underbrace{\frac{d|u_{\vec{k}i}\rangle}{d\vec{k}}} - \frac{d\langle u_{\vec{k}i}|}{d\vec{k}} \frac{d|u_{\vec{k}i}\rangle}{d\lambda} \right] =$$

INTEGRATING BY PARTS WITH RESPECT TO $\lambda$ THE PRODUCT

$$= -2|e| i \int \frac{d^3k}{(2\pi)^3} \left\{ \sum_i^{occ} \left[ \langle u^{\lambda_A}_{\vec{k}i} | \frac{d|u^{\lambda_A}_{\vec{k}i}\rangle}{d\vec{k}} - \langle u^{\lambda_B}_{\vec{k}i} | \frac{d|u^{\lambda_B}_{\vec{k}i}\rangle}{d\vec{k}} \right] \right.$$

$$\left. - \int_{\lambda_B}^{\lambda_A} d\lambda \underbrace{\left[ \langle u_{\vec{k}i} | \frac{d}{d\lambda} \left[ \frac{d|u_{\vec{k}i}\rangle}{d\vec{k}} \right] + \frac{d\langle u_{\vec{k}i}|}{d\vec{k}} \frac{d|u_{\vec{k}i}\rangle}{d\lambda} \right]} \right\}$$

$$\underbrace{\frac{d}{d\vec{k}} \Bigg[ \underbrace{\langle u_{\vec{k}i} | \frac{d|u_{\vec{k}i}\rangle}{d\lambda}}_{\text{FUNCTION PERIODIC IN } \{\vec{G}\} \text{ SPACE}} \Bigg]}_{\text{TOTAL DERIVATIVE OF A PERIODIC FUNCTION}}$$

$$\int_{\text{PERIODIC CELL}} d^3k \, \frac{d}{d\vec{k}} \Big( \underbrace{f(\vec{k})}_{\text{CELL PERIODIC}} \Big) = 0 \, !$$

$$\Downarrow$$

$$\boxed{\vec{P}(\lambda_A) = -2|e| \int \frac{d^3k}{(2\pi)^3} \sum_i^{occ} i \left\langle u_{\vec{k}i}^{\lambda_A} \middle| \frac{d\, u_{\vec{k}i}^{\lambda_A}}{d\vec{k}} \right\rangle}$$